

IV.J.4 Advanced Catalysts for Direct Methanol Fuel Cells

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Objectives

- Demonstrate the feasibility of reducing noble metal catalyst loading to less than 0.5 mg/cm² for direct methanol fuel cells.
- Identify potential non-noble metal anode catalysts for the electro-oxidation of methanol.

Technical Barriers

This project addresses the following technical barrier from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- O. Stack Material and Manufacturing Cost

Approach

- Develop a methodology that provides high-throughput fabrication and analyses of novel alloy materials of arbitrary composition.
- Evaluate multi-component alloys consisting of platinum, ruthenium, nickel and zirconium that are corrosion-resistant in acid for catalytic activity.
- Analyze results of polarization studies to develop a rationale for catalyst performance.
- Evaluate promising materials in full direct methanol fuel cells.

Accomplishments

- Developed a technique for combinatorial sputter-deposition and evaluation of multi-component corrosion resistant and catalytic materials. This combinatorial approach allows for the preparation and evaluation of thirty-six samples simultaneously, allowing for rapid screening of formulations. The alloy films had surface and bulk compositions that were identical, allowing for accurate materials properties quantification.
- Prepared and evaluated a wide range of quaternary compositions consisting of platinum, ruthenium, nickel and zirconium in half-cells.
- Demonstrated that Ni₃₀Zr₁₃Pt₃₃Ru₂₃ is as active as optimized PtRu (nominally found to be Pt₈₄Ru₁₆).
- Demonstrated that electronic effects can be exploited to achieve higher activity.
- Arranged for fabrication of full fuel cells (to be fabricated in the fourth quarter of FY 2004).

Future Directions

- Develop fundamental principles for catalyst design based on combinatorial data. This will be applicable to hydrogen/oxygen chemistry.

- Extend investigation to new compositions involving cobalt instead of nickel.
- Scale-up and demonstrate in large membrane-electrode assemblies and stacks for durability testing.

Introduction

The direct methanol fuel cell (DMFC) is very attractive because of the simplicity of the overall design and the relative ease with which a high-energy fuel such as methanol can be stored in liquid form. However, DMFCs currently require unsupported noble metal catalysts at high loadings of 2.5 – 4.0 mg/cm², leading to a high catalyst cost of \$100-150/kW. Also, to keep the overall fuel cell cost low, the catalyst application must be readily suitable for manufacturing. Thus, cost represents a major obstacle to commercialization of DMFCs. It is also critical to increase the overall fuel cell efficiency to meet the weight and volume requirements for transportation applications. The present research effort aims at addressing these key issues of cost and efficiency. The ultimate objective is to develop new low-cost electro-catalyst materials and new methods of preparing fuel cell electrodes that will reduce the amount of noble metal used and lead to overall cost reduction and improved performance of direct methanol fuel cells. Another objective of this effort is to develop principles for catalyst design based on electronic properties of constituent materials. These methods and materials could also be applicable to hydrogen-air fuel cells.

Approach

Multi-component alloys of virtually any composition can be readily prepared as thin films by sputter deposition. Earlier efforts at JPL have shown that corrosion-resistant compositions based on nickel and zirconium can be sputter deposited, and that sputter-deposited catalysts can function competitively in a DMFC.¹ Also, nickel and zirconium with unfilled d-electron shells can be used to alter the electron density around noble metals such as platinum and ruthenium. Therefore, multi-component alloys, containing Ni, Zr, Pt, and Ru, that are catalytically active and stable in the fuel cell environment were investigated. In order to correlate the catalytic activity of these materials with their surface composition and electronic state, it is important that variations resulting from differences in morphology, surface area, surface vs. bulk

composition, and number of grain boundaries be identified. This was achieved by depositing thin (~10 nm) films that are nearly amorphous. The variation in the catalytic activity measured for such deposits can then be attributed to the surface composition. The structure and composition of the deposited samples were analyzed using X-ray diffraction (XRD), Rutherford Backscattering (RBS) and energy dispersive analysis of X-Rays (XEDS). In order to rapidly screen samples, a multi-electrode array was developed to allow for the simultaneous electrochemical evaluation of up to thirty-six different compositions.

Results

Materials Preparation and Analyses

A combinatorial sputter-deposition technique that is based on co-sputtering of metals has been developed and tested. In a typical arrangement, the substrate and targets are placed in a sputter chamber as shown in Figure 1. The various cells on the substrate had a composition related to their spatial relationship to the target. This provided a wide compositional range of alloys that were simultaneously created under identical deposition conditions. The resulting alloy films were typically less than 100μ thick, and did not exhibit any compositional discrepancy between the surface and the bulk of the film. This is a result of the fast deposition time (~1 minute) and low substrate temperature (25°C), and is critical to developing principles for catalyst design. The 36-electrode substrate/current collector structure is shown in Figure 1(b). Using this test structure, the new catalyst alloys were studied in parallel using a custom-made 36-channel pseudo-potentiostat, modified from a well characterized design.² Figure 1(d) shows a planar view of the nominal relative positions of the electrodes and the sputter targets.

Combinatorial Electrochemical Studies

Figure 1(c) is an image of the combinatorial test set-up. The test solution consisted of a 1 M H₂SO₄/1M methanol solution held at temperatures ranging

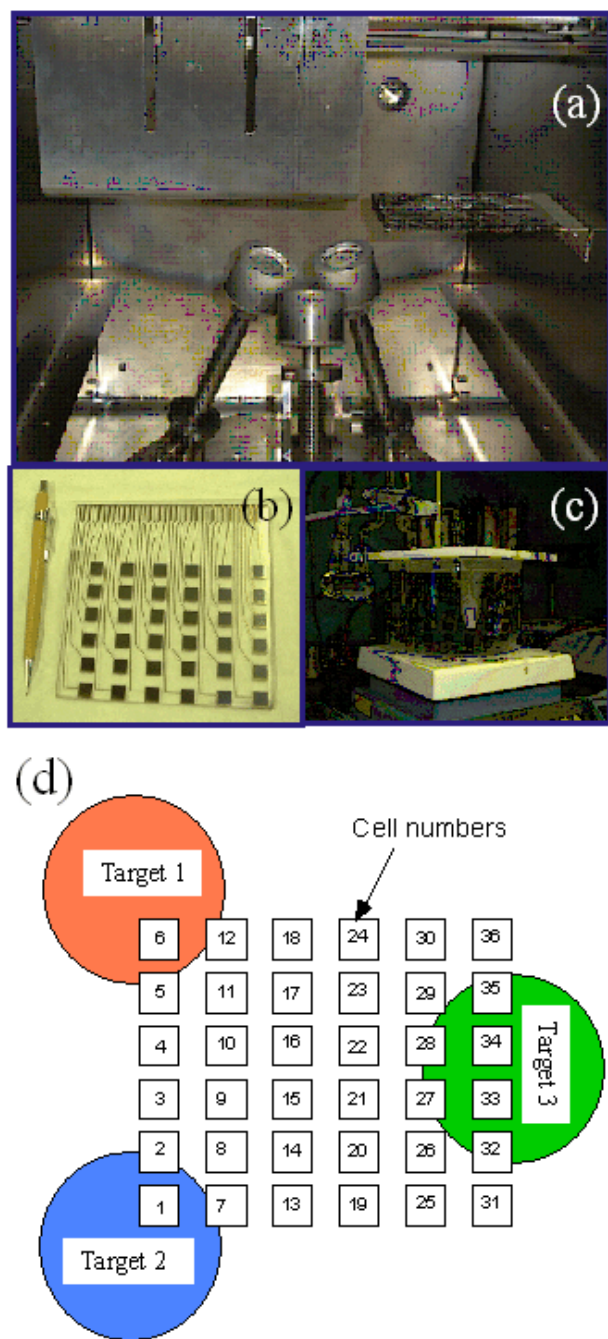


Figure 1. (a) Image of Sputter Chamber Interior - Three 2" Sputter Targets are Oriented Towards the Substrate Holder (b) Image of 36 Electrode Au Current Collector Array On 5" X 5" Glass Plate (c) Image of Electrochemical Test Set-Up (d) Schematic of Planar View of Nominal Relative Position Of Sputter Targets and Test Cells as Defined by a Stainless Steel Physical Mask During Deposition

from 25 to 60°C. Cyclic voltammetry (CV) and potentiostatic (PS) studies were conducted on all electrodes. The CV scans consisted of 3 repeated scans ranging from 0.1 to 0.8 V vs. RHE (reversible hydrogen electrode) at a rate of 5 mV/sec, while the PS data was collected by holding all electrodes at 0.45 V vs. RHE for 300 seconds. Two representative alloy depositions will be discussed in this report: Pt/Ru (with greater than 70 atomic % Pt) and Ni/Zr/Pt/Ru with less than 50 atomic % Pt. CV data collected at 54°C from the Pt/Ru sample set is shown in Figure 2(a). Electrode performance varies smoothly from cell to cell, with the highest current densities in cells 15 and 16. The PS data for this alloy set at two different temperatures are shown in Figure 2(b). The highest current densities were for, once again, cells 15 and 16 for both 25 and 54°C. Compositional analyses (x-ray energy dispersive spectroscopy, RBS) showed that the best composition was nominally a Pt/Ru atomic ratio of 86/14.

Similar data from the Ni/Zr/Pt/Ru quaternary system are shown in Figures 3(a) and 3(b). In this case, the highest performing catalyst was found in cell #4, which had a composition of approximately $\text{Ni}_{31}\text{Zr}_{13}\text{Pt}_{33}\text{Ru}_{23}$. The potentiostatic current density produced using this alloy was nearly that of the best Pt/Ru alloy.

Structural Analyses

Figure 4 shows x-ray diffraction data (XRD) of selected Pt/Ru and Ni/Zr/Pt/Ru alloys. The data in Figure 4(a) show that the Pt/Ru films had well resolved FCC structure consistent with the well-characterized Pt/Ru solid-solution system.³ Conversely, Figure 4(b) shows that the Ni/Zr/Pt/Ru alloy had a mixed-phase/amorphous structure that did not have a well-resolved set of diffracted peaks.

Conclusions

A method for synthesizing and testing novel fuel cell catalyst alloys of virtually any composition has been developed. To establish the viability of this approach, the Pt/Ru system (for DMFC anode use) was studied, with results showing that the best Pt/Ru ratio was nominally 84/16. This result is similar to that found in a number of other studies that used

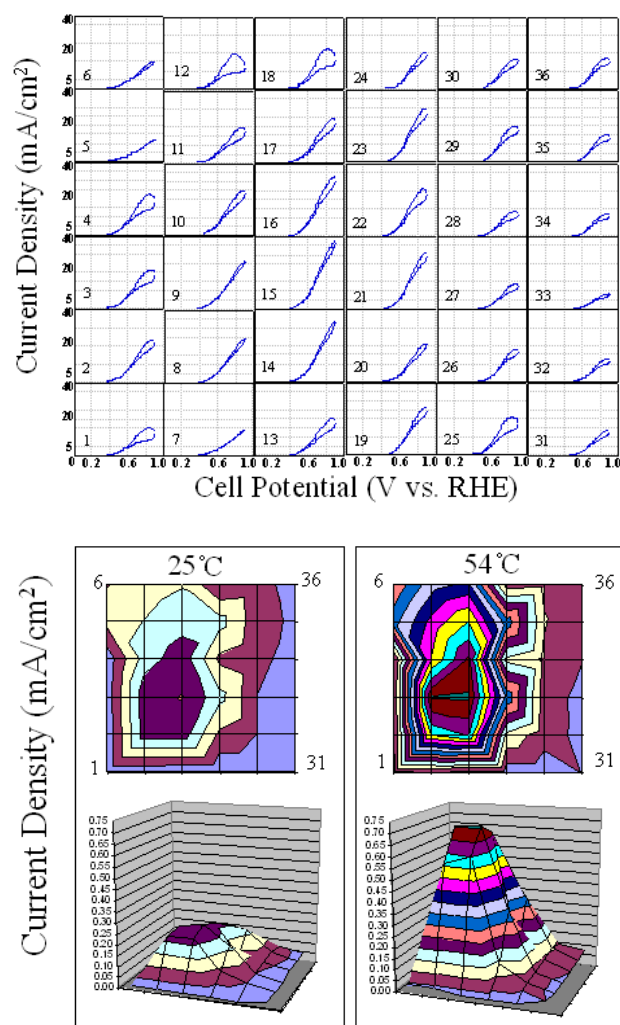


Figure 2. (a) CV Data Collected from 36 Electrode Pt/Ru Test Structure at 54 °C - The Cell # is Indicated in the Lower Left of Each CV Plot. (b) 3-D Topographical Representation of PS Data from 25 and 54 °C from the Same Electrode Set - All Cells Were Kept at 0.45 V vs RHE for 300 Seconds

syntheses routes resulting in smooth, well-characterized catalyst surfaces.^{4,5,6}

These result are in contrast to other studies that have focused on industrial Pt/Ru powders, where the actual catalyst surface composition was not directly and independently determined.⁷

A novel quaternary alloy, NiZrPtRu was then examined. It was found that the PS current levels produced by the best NiZrPtRu alloy (with about 33

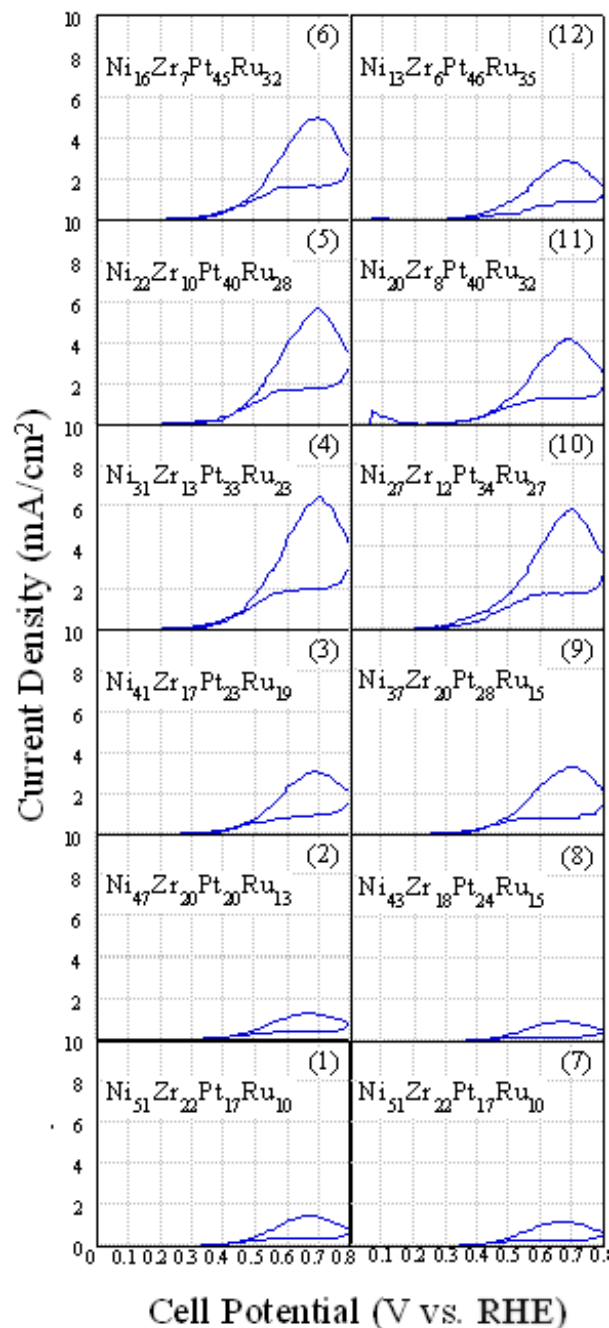


Figure 3. (a) CV Data From a Ni/Zr/Pt/Ru Set of Cells Collected At 35 °C - Only Cells 1-12 Yielded Significant Current Density

atomic % Pt) were comparable to those found in the best Pt/Ru alloys. This result is depicted in Figure 5, which shows the PS current densities for various alloy compositions at temperatures ranging from 25 to 60 °C. Figure 5(a) is the raw data, while Figure

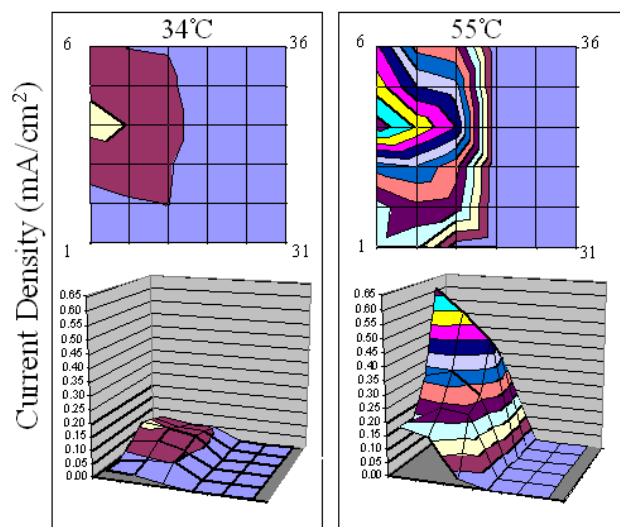


Figure 3. (b) PS Data from the Same Electrode Set - All Cells Were Kept At 0.45 V vs RHE for 300 Seconds (Alloy composition is indicated for each of the test cells.)

5(b) is normalized to mole fraction Pt. A key result is that Pt usage for the NiZrPtRu alloy is significantly higher than that observed in the Pt/Ru system. XRD data showed that the NiZrPtRu alloy did not have a well-defined crystal structure, in contrast to the Pt/Ru alloy. These data combine to show that a novel catalyst system has been discovered that has a unique structure (multi-phase/amorphous). This allows for a significant increase in Pt utilization, resulting in a substantial decrease in the amount of Pt needed to make viable DMFCs at any scale. This is consistent with the idea that this new alloy possesses an atomic/electronic structure that is fundamentally different from that found in the traditionally used Pt/Ru system. Though this result is significant, we feel that it represents only a step towards the ultimate goal of understanding catalyst processes and eventually eliminating the need for noble metal content completely.

References

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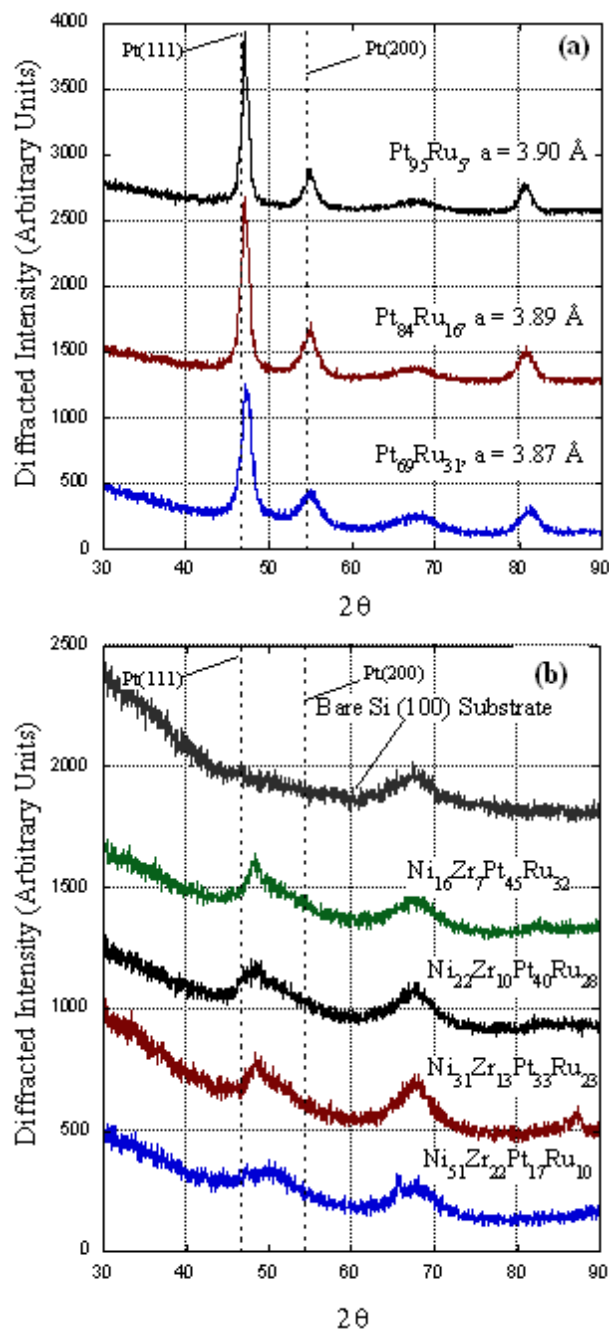


Figure 4. X-ray Diffraction from Selected Alloy Compositions

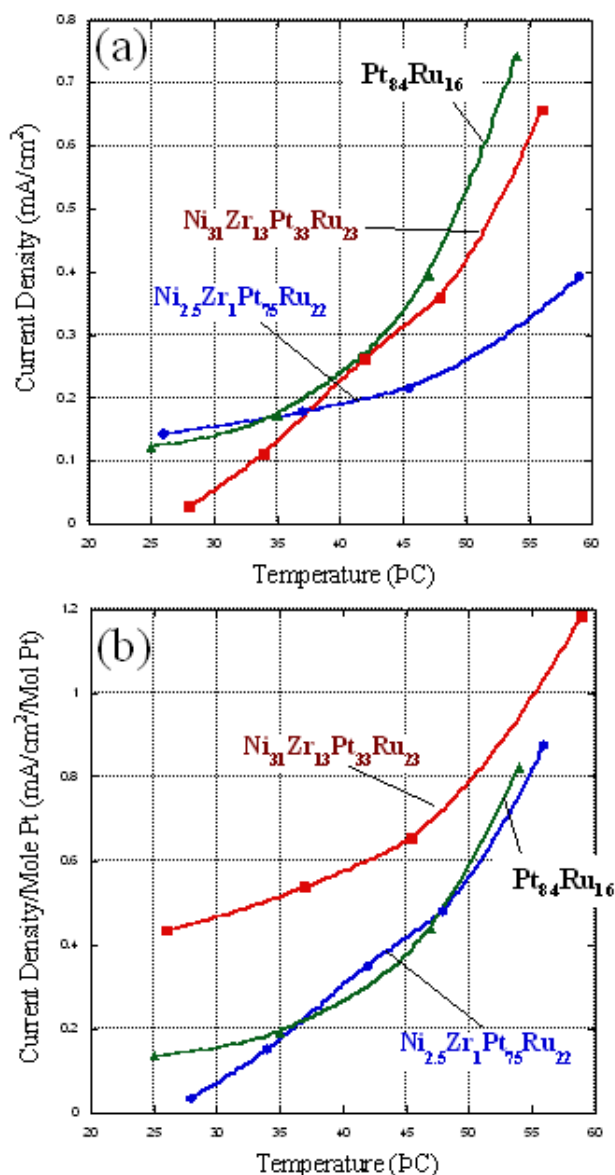


Figure 5. (a) PS Data From Three Selected Alloy Systems Over a Range of Temperatures (b) Same Data Normalized to Mole Fraction Pt

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FY 2004 Publications/Presentations

1. Invited Presentation: Sputter-Deposited Anode Catalysts for Direct Methanol Fuel Cells, Knowledge Foundation 6th annual international symposium, Small Fuel Cells 2004, May 5-7, Arlington VA.
2. DOE Hydrogen Program Review, May 2004.
3. "Fuel Cell Catalyst Discovery Using Combinatorially Co-Sputtered Nanoscale Thin Film Electrodes", Jay F. Whitacre, S.R. Narayanan, Manuscript submitted to *J. Electrochemical Society*, August 2004.

Special Recognitions & Awards/Patents Issued

1. "A Low Pt Content Direct Methanol Fuel Cell Anode Catalyst: Nanophase PtRuNiZr", Provisional patent application, Caltech, May 2004.

